FORMATION OF A POROUS STRUCTURE OF FOAM SILICATES BASED ON LIQUID-GLASS COMPOSITIONS

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The influence of various additives on the porization of liquid-glass compositions using new approaches for analyzing experimental data, making it possible to obtain a quantitative assessment of the influence of inorganic additives and salts, is determined. Application of the law of constancy of the volume phase composition of dispersed systems makes it possible to express mathematically the influence of technological parameters (temperature, time) and the form of the types of additives introduced on the porization processes in such compositions.

Liquid glass based on soluble silicates of alkali metals is a unique material which when heated up to 150 – 500°C is capable of forming solid inorganic foam. Heating partially dried liquid-glass granules or compositions in molds with a closed volume permits obtaining heat-insulation materials with a rigid porous structure, occupying an intermediate position with respect to functional properties between cellular concretes and foam glass. This material can be called, with full justification, a foam silicate based on liquid glass.

Liquid glass compositions (LGC) are obtained by mixing liquid sodium glass with specific additives, which can be divided into several groups according to the effect on the liquid glass and the material being fabricated:

1) inert with respect to liquid glass, acting as a framework forming filler in the finished article;

2) gel-forming, giving rise to the gel-forming reaction in liquid glass and thereby destroying its polymer structure;

3) thermoreactive additives, which do not interact with liquid glass and decompose on heating, releasing gaseous products.

The effect of group-I additives depends on the nature of the substance and the dispersity. As the additive enters the LGC composition without destroying the colloidal structure of the liquid glass itself, it will have an ordering effect on the macrostructure of the heat-insulating material and increase the physical – mechanical properties of the article. When the volume content of the additive exceeds the maximum value for a given substance, the liquid glass coagulates with water being released and a silica gel being formed, which has a negative effect on the swelling capacity of LGC. Examples of such additives are finely dispersed quartz sand, tripoli, diatomite, dehydrated limonite (Fe_2O_3), MgO, and CuO.

The group-II gel-forming substances are introduced into GLC to increase the viscosity of LGC rapidly and increase process efficiency — it is easier to regulate the gel obtained and to pack it in molds. However, when the gelling agent content is significant, the polymer structure of the liquid glass breaks down and the porization capacity of the glass decreases, and the density of the articles correspondingly increases and their heat-insulation properties decrease. Thus, these additives must be introduced in small, strictly determined, quantities. Examples of well-known gelling agents are sodium silicofluoride, ethyl alcohol, boric acid, and many water soluble salts of alkali-earth and heavy metals. Solutions of alkali-metal salts, for example, NaCl, KNO_3, $NaHCO_3$, and Na_2SO_4, introduced in substantial quantities into the composition, will also give rise to gel formation [1].

Thermoreactive additives (group III) are substances which are insoluble in alkali silicates and do not enter into appreciable volume interaction with them at normal temperatures, while on heating these additives do enter into chemical interaction with alkali silicates, participating in the formation of a water-insoluble material of pore barriers, and often decompose with gaseous products being released, which promotes the porization process. Examples of such substances are calcium carbonate $CaCO_3$, magnesium carbonate $MgCO_3$, limonite FeOOH, malachite $CuCO_3 \cdot Cu(OH)_2$, magnesium carbonate, and others.

It should be noted that many substances used as additives in LGC have a complicated effect and occupy an intermediate position in the classification proposed above.

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Our objective in the present work is to determine the effect of different additives on the porization of LGC using new approaches for analyzing the experimental data, making it possible to obtain a quantitative assessment of the effect of inorganic additives and salts on the porization capacity of LGC.

Special methods must be used to determine the optimal parameters of the technological process for obtaining foam silicate materials in order to monitor the volume phase composition of the system, undergoing porization, in the initial, instantaneous, and final states. These methods are based on the law of constancy of the phase composition: at any moment in time the sum of the volume fractions of the solid, liquid, and gaseous phases of the system is constant and equal to 1 irrespective of the form of the dispersed system or structure or the form and magnitude of the energy input.

This law is expressed mathematically as follows:

$$K_{\text{sol1}} + K_{\text{liq1}} + K_{\text{gas1}} = K_{\text{sol2}} + K_{\text{liq2}} + K_{\text{gas2}} = ... =$$
$$K_{\text{sol } n} + K_{\text{liq } n} + K_{\text{gas } n} = 1,$$

where K_{sol}, K_{liq}, and K_{gas} are the volume content of the solid, liquid, and gaseous phases of the system at the corresponding process stage [2].

A parameter n characterizing the intensity of structure-forming processes in dynamical systems can be obtained on the basis of this law. It shows the relative change in the ratio of the volume concentration of the solid phase and the free pore space at a transition of the dispersed system from one state to another under the influence of an external energy action (chemical, mechanical, or thermal). The quantity n can be determined from the relation

$$\frac{K_{\text{sol2}}}{1 - K_{\text{sol2}}} = n \frac{K_{\text{sol1}}}{1 - K_{\text{sol1}}},$$

where K_{sol1} and K_{sol2} are the volume fractions of the solid phase at the start and end of the porization of the system.

If no changes occur in the system, then $n = 1$. A decrease of the volume of the system is characterized by $n > 1$ and an increase of volume (porization) is characterized by $n < 1$. If the change in the parameter n is normalized in the range $0 - 1$, then on porization the degree of rearrangement of the structure of the material can be determined according to the formula

$$\alpha_n = \frac{1/ n_i - 1}{1/ n_i} = 1 - n_i,$$

where $1/n_i$ is the degree of swelling of the material during the process or at the end of the action on the dispersed system; $1/n_i = V_2 /V_1$ (V_2 and V_1 are the volumes of the system in the final and initial states, m^3).

It is evident from the last relation that the larger the value of the parameter α_n characterizing the transition of the system from the initial into the final state, the more intense the porization process in a given system and the more intense the

restructuring of the material are; this parameter can be used as a dependent variable in kinetic studies. In addition, an important technological conclusion follows from the relations presented above: the higher the volume concentration of the solid phase in the initial material, the more intense the porization process is [2, 3].

A second important prerequisite for obtaining foam silicate with optimal characteristics is satisfaction of the principle of correspondence between the rate of physical – chemical processes in which moisture is released and evaporated and the rate of formation of the new structure of the material (porization).

The influence of various additives and fillers on the porization of LGC was assessed by means of kinetic studies. Using the degree of restructuring as the dependent variable, a comparative analysis can be made of different LGC compositions and the rate constants and activation energies of porization processes can be calculated taking account of the initial and final states of the system.

The kinetics of the LGC porization was investigated using a Shill apparatus [4] modified for use with foam silicate materials.

An LGC consisting of liquid glass (with silicate modulus $m = 3$, moisture content 55%, and density 1500 kg/m^3) and additives was used to prepare the experimental samples. The additives and fillers for preparing LGC were determined on the basis of the classification presented above and the experimental data. Finely milled limestone, magnesium oxide, brown iron ore in dehydrated and hydrated forms, malachite $CuCO_3 \cdot Cu(OH)_2$, and calcined malachite CuO were used as fillers.

The compositions with calcined (up to 500°C) and uncalcined fillers were prepared to estimate the contribution of the additions of gaseous products of decomposition to the total porization. The mass content of the filler introduced was 10%. The salts Na_2CO_3, $NaNO_3$, K_2SO_4, $NaCl$, KNO_3, $NaHCO_3$, K_2CO_3, and Na_2CO_4 were introduced in amounts equal to $0.5 - 1.0\%$ of the total mass of the liquid glass. The salts added to LGC not only release gaseous products on heating and decomposition but they also have a positive effect on the LGC formation stage. When fillers and salts are added simultaneously to the LGC composition, the salts partially blocked the development of ion-exchange processes between the filler and the liquid glass; this makes it possible to increase the porization capacity of the LGC as a whole.

The LGC obtained was poured into cylindrical plastic containers using an extruder. When a 15 mm in diameter and $2 - 3$ mm high sample acquired adequate strength and hardness, it was extracted from the container and the initial parameters K_{sol1} and K_{liq1} were determined.

Porization of the samples was performed as follows. The shell case of the apparatus with a measuring rod was placed into a laboratory shaft furnace, and the furnace and apparatus were heated up to a prescribed temperature — 300, 350, 400, and 450°C. Next, a disk-shaped sample was placed into a

TABLE 1.

Composition	Additive to liquid glass	Additive mass content, %	Porization rate		E_{p1}, kJ/mole	E_{p2}, kJ/mole
			1 section, $\Delta\alpha/\Delta\tau \times 10^2$	2 section, $\Delta\alpha/\Delta\tau \times 10^4$		
1	No additives	–	2.51	4.40	24.57	36.25
2	Limonite	10.0	3.16	0.62	18.29	49.55
3	Calcined limonite	10.0	3.38	0.61	14.90	36.25
4	Malachite $CuCO_3 \cdot Cu(OH)_2$	10.0	3.25	0.54	28.60	61.23
5	Calcined malachite CuO	10.0	3.55	1.34	20.94	37.47
6	Limestone $CaCO_3$	10.0	3.10	1.04	29.35	66.76
7	MgO	10.0	3.11	0.90	16.52	35.86
8	KNO_3	0.5	3.13	0.38	21.29	92.22
9	Na_2CO_3	0.5	3.32	0.88	13.30	35.05
10	Na_2SO_4	0.5	3.35	0.60	16.17	45.07
11	$NaNO_3$	0.5	3.27	0.37	15.71	39.61
12	K_2SO_4	0.5	3.03	0.25	22.50	98.83
13	K_2CO_3	0.5	3.18	0.22	21.18	81.95
14	$NaHCO_3$	0.5	3.23	0.50	22.10	51.56
15	NaCl	0.5	3.25	0.46	17.72	42.70

shell case and the rate at which the measurement rod rose was noted on a millimeter scale. The temperature field was stabilized in 2 – 3 min from the start of the experiment, while the entire porization process took 10 – 20 min. The values of the parameters $K_{sol\,i}$, Π_i, n_i, and α_{ni} were calculated using the data obtained.

Analysis of the experimental data made it possible to determine the general laws of porization processes. A porization process consists of three basic stages whose duration and character depend on the form and quantity of the moisture contained in the material:

first stage — heating of the material up to 100 – 120°C; in this interval the initial solid material passes into a pseudo-pyroplastic state and starts to deform intensively with volume increasing;

second stage — at 130 – 150°C intense release of free and adsorbed water occurs, and intense porization of the material is observed ($\alpha_n = 0.7 – 0.8$);

third stage — at temperatures above 150°C the constitutional water is removed, final restructuring occurs, and the physical – chemical processes are completed (α_n up to 0.99).

Analyzing the data obtained and the macrostructure of the samples shows that when the structure of the article with maximum uniformity is formed, the constitutional water, whose removal starts at temperatures above 100 – 120°C, while removal of excess adsorption water results in the formation of large through pores and channels in the material, makes the main contribution. Consequently, the initial LGC must contain the lowest possible amount of free and adsorption water.

The influence of different additives and fillers on the LGC porization process is illustrated in Table 1.

The data were analyzed using the following equation [2]:

$$\alpha_n = 1 - e^{-k\ln\tau}e^b \quad \text{or} \quad \ln(1 - \alpha_n) = -k\ln\tau + b,$$

where $0 < \alpha_n < 1$, k is the rate constant for porization of the structure (sec^{-1}), τ is the duration of the process (min), and b is a coefficient.

The kinetic data were used to construct a plot in the coordinates $\ln(1 - \alpha_n) = f(\ln\tau)$. The characteristic curves are presented in Fig. 1. The following regularities are evident:

lowering the porization temperature increases the onset time of the porization process;

for a sample consisting of pure liquid glass the curves are straight lines, while introduction of a salt additive or filler results in the appearance of two sections on the kinetic curves with different slope angles with respect to the time axis.

The apparent activation energy of the porization process in all LGC was determined by the method of iso-ordinate sections [5] using the following relation:

$$E_p = \frac{R(\ln\tau_1 - \ln\tau_2)}{1/T_1 - 1/T_2},$$

where E_p is the apparent activation energy of the porization process (kJ/mole), $R = 8.314$ J/(mole · K) is the universal gas constant, and τ_1 and τ_2 are the times at which the values of α_{ni} at the temperatures T_1 and T_2 are reached ($T_1 = 573$ K, $T_2 = 723$ K).

The value of E_p for salt additives was calculated for $\alpha_n = 0.8$ and 0.985 and in the case of 10% filler content at $\alpha_n = 0.8$ and 0.97. These values of α_n were chosen because of the presence of two rectilinear sections with different

porization mechanisms and, correspondingly, different values of E_p.

The porization rate was estimated from the degree α_n of structural change in time on the two sections. At the first stage free and adsorption water is removed, and thermal destruction of additives occurs; this process is characterized by higher rates than that of the second stage, at which residues of chemisorption water and gaseous products from the destruction of the additives and fillers are removed by diffusion.

Analyzing the data, it is possible to assess the influence of the additives on the porization capacity of LGC. For example, the porization rate on the first section for compositions with additives consisting of mineral fillers and salts ranges from 2.9×10^{-2} to 3.4×10^{-2} sec^{-1}, while the porization rate of pure liquid glass is lower at this stage — 2.5×10^{-1} sec^{-1}. This can be explained by an increase in the amount of free and adsorption water in LGC when the additives are introduced. At the second stage the porization rates of compositions with additives lie in the range $(0.2 - 1.5) \times 10^{-4}$ sec^{-1} with the porization rate of pure liquid glass 4.4×10^{-4} sec^{-1}, which indicates a decrease of the porization capacity of LGC with mineral fillers, but such fillers, just as conditions of alkali salts, promote formation of a more uniform porous structure of the articles.

The range of values $E_p = 13 - 35$ kJ/mole on the first section characterizes the process accompanied by breaking of hydrogen bonds in the liquid glass, and for $E_p > 35 - 40$ kJ/mole on the second section — the development of viscous flow with porization of the system. The low value of E_p at the first stage of porization is due to the participation of a substantial amount of the gas phase (water vapor) in the porization process. In pure liquid glass water enters its polymer structure, and all water in the system is removed more uniformly, while the introduction of additives and fillers into LGC causes partial decomposition of the liquid glass with release of silica gel and transition of water from the adsorption and chemisorption states into a free state. This can explain the existence of two sections with different values of E_p. Comparing the values of E_p for the porization of LGC with compositions Nos. 2 and 3 and also Nos. 4 and 5 (see Table 1) permits estimating the contribution of the decomposed thermoreactive additive to the porization of compositions. The higher the value of E_p characterizing the porization process, the larger the effect of a temperature change on this process is. Analysis of the data in Table 1 permits drawing an important technological conclusion: for porization of LGC it is desirable to use additives which permit reaching at the second stage of the kinetic curve the values $E_p > 50$ kJ/mole. A uniform and quite rigid foam silicate structure is formed in this case.

The law of constancy of the volume phase composition of a dispersed system makes it possible to construct a graphical representation in the coordinates K_{liq}, K_{sol}, and K_{gas} of the porization process in LGC, associated with a change in the phase composition of the system. The porization of LGC
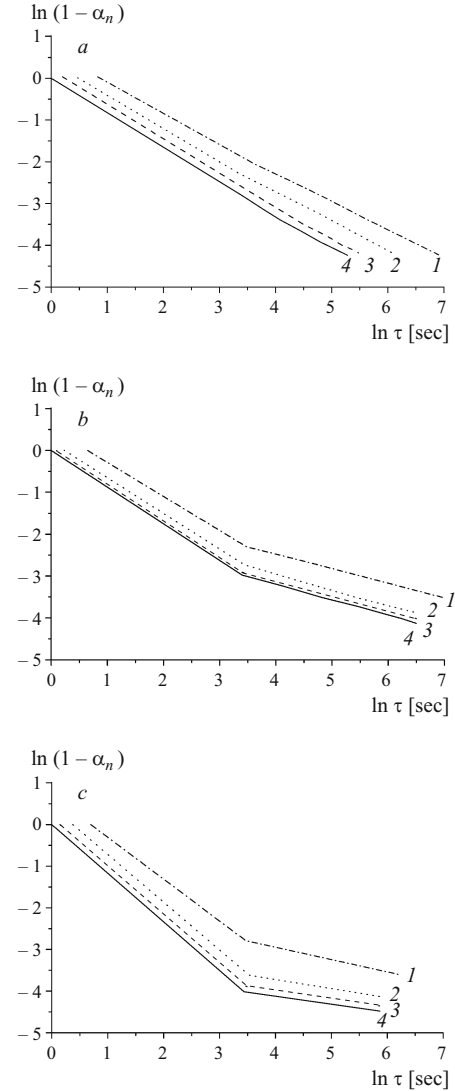

Fig. 1. Porization kinetics of liquid glass with no additives (*a*), LGC with 10% limonite (*b*), and LGC with 0.5% KNO$_3$ added (*c*): *1*, *2*, *3*, and *4*) 300, 350, 400 and 450°C, respectively.

occurs, schematically, along the straight line connecting the initial point of the LGC composition on the $K_{liq} - K_{sol}$ side and the vertex K_{gas} (Fig. 2). When the volume of the system ceases to increase, the line representing the process is oriented parallel to the $K_{liq} - K_{gas}$ side up to intersection with the $K_{sol} - K_{gas}$ side; this corresponds to the phase composition of the final state of the system.

The change in the thermal conductivity of a material during porization can be predicted from the known phase composition using the following relation:

$$\lambda_m = \frac{K_{sol1}}{1 - K_{sol1}} = \frac{1}{\dfrac{K_{sol\,i}}{\lambda_{sol}} + \dfrac{K_{liq\,i}}{\lambda_{liq}} + \dfrac{K_{gas\,i}}{\lambda_{gas}}},$$

where λ_{sol}, λ_{liq}, and λ_{gas} are the thermal conductivity of the solid, liquid, and gaseous phases, respectively;
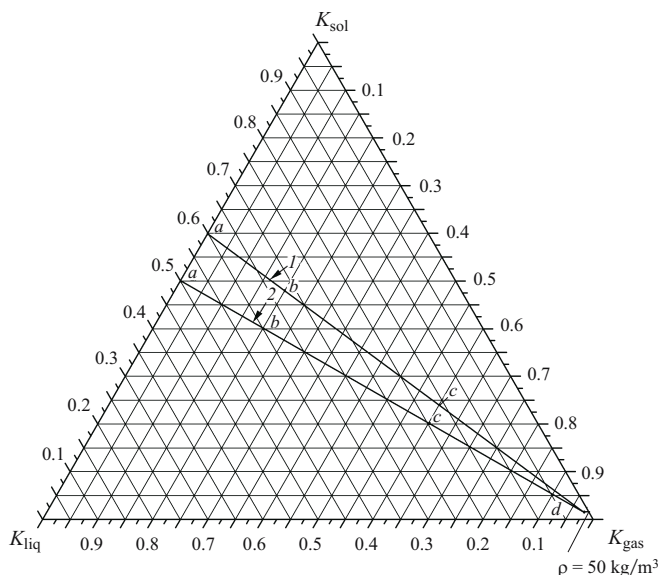
Fig. 2. Phase diagram of the porization of LGC.

Line	Thermal conductivity, W/(m · K), with K_{gas}			
	0	0.2	0.6	0.97
1	1.285	0.171	0.064	0.026
2	1.250	0.113	0.041	0.027

In summary, the use of volume phase characteristics facilitates the study of porization processes in dispersed systems and makes it possible to extract valuable information concerning the mechanism of the processes occurring. The law of constancy of the volume phase composition of dispersed systems makes it possible to express mathematically the effect of technological parameters (temperature, time) and the form of the additives introduced on the process of porization of liquid glass compositions.

Heat-insulating construction materials with a rigid porous structure can be obtained from foam silicate based on liquid-glass compositions.

$\lambda_{sol} = 1.2$ W/(m · K), $\lambda_{liq} = 0.6$ W/(m · K), and $\lambda_{gas} = 0.0255$ W/(m · K), which values are based on data provided in reference handbooks; K_{sol1} is the initial content of the solid phase (arb. units); $K_{sol\,i}$, $K_{liq\,i}$, and $K_{gas\,i}$ are the instantaneous values of the volume fractions of the solid, liquid, and gaseous phases (arb. units).

The thermal conductivity at the characteristic points $K_{gas} = 0$, 0.2, 0.6, and 0.97 (the points *a*, *b*, *c*, and *d*, respectively) was calculated using the relations presented above for compositions with $K_{sol1} = 0.5$ and 0.6 (lines *1* and *2*). The data obtained are presented in Table 2.

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